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13. ABSTRACT (Maximum 200 words)  We summarize our studies of the chemical, photophysical, optical limiting, and other nonlinear optical properties of long wavelength-absorbing azulene derivatives; namely, fluorinated azulenes, azulenic donor-acceptor molecules, and reverse saturable absorber azulenic symmetrical dye chromophores. The effect of fluorine and other substituents on the excited singlet state properties of azulene and, in particular, the enhancement of first excited state lifetimes and fluorescence quantum yields was investigated. Both Hyper-Raleigh Scattering and Resonance Raman measurements of azulenic donor-acceptor chromophores revealed the involvement of more than one excited state in the lowest energy electronic transitions contrary to accepted models. An ultrafast transient absorption spectroscopic study of a series of guaiiazulenic polymethine dyes indicated the presence of several discrete short-lived excited singlet state species that absorb over the entire visible region. A ring-locked azulenic dye dimer formed at low temperature and was studied by variable temperature NMR. Optical quality polymer films of azulenic dyes were prepared by doping and, in one case, by a novel chemical transformation of the polymer host. Unexpected thermochromic behavior was observed for a trimethine dye. A novel series of cross-conjugated azulene derivatives, potentially useful as two-photon absorbers, was also prepared.				
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## Introduction

Azulene has piqued the curiosity of scientists for many years due to its singularly most striking property – it is brilliantly blue (hence, the name derived from “azure”). In contrast, the aromatic hydrocarbon naphthalene is completely colorless even though both molecules have the same chemical composition ( $C_8H_{10}$ ) and are isoelectronic (5 double bonds and two fused rings each). It turns out that the color of azulene is primarily due to an unusually low  $S_1$  energy together with an unusually large  $S_1 \leftarrow S_2$  gap. The absorption spectrum of azulene features a window of transparency ( $\sim 400$ - $500$  nm) sandwiched between the rather broadened, low-lying  $S_1$  band ( $500$ - $700$  nm) and the higher energy  $S_2$  band  $< 400$  nm. Interestingly, the dipole moment for azulene in  $S_1$  is reversed relative to  $S_0$  with considerable charge build-up in the seven-membered ring.

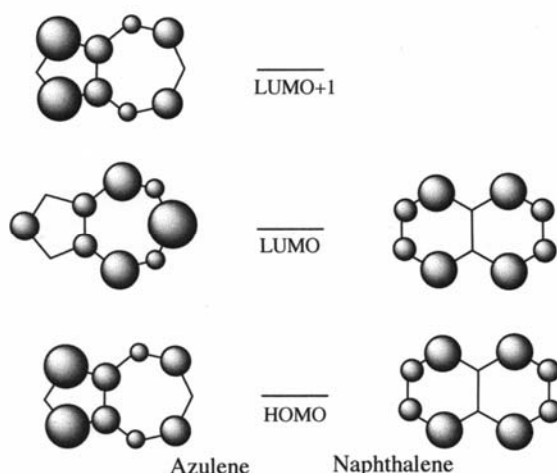


Figure 1. Probability of locating an electron (square of coefficients of the wave-functions) in the HOMO, LUMO and LUMO + 1 of azulene (left) and naphthalene (right).

The stabilization of  $S_1$  is clearly associated with greatly diminished electron-electron repulsion in  $S_1$  relative to  $S_0$ . Azulene also has a surprisingly large ground state dipole moment (1 Debye) that suggests the involvement of resonance stabilization; i.e., the formation of Hückel aromatic tropylium carbocation and cyclopentadienide carbanion. The second excited state electron distribution resembles the ground state.

Utilization of the novel ground and excited state electronic properties of azulene is the key for controlling the fluorescence and nonlinear optical properties of azulene-containing chromophores by molecular engineering.

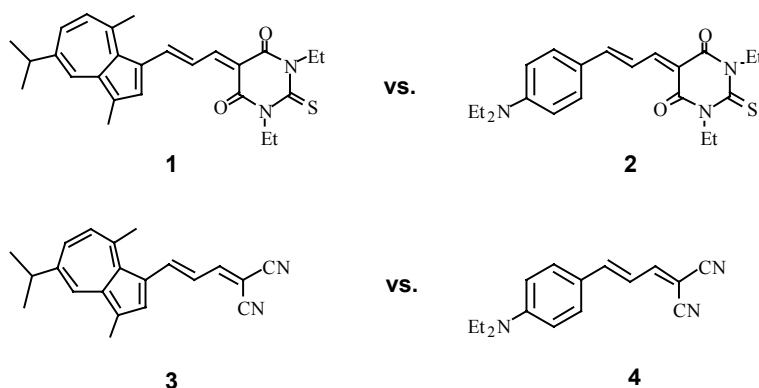
### Research Objectives

We had previously demonstrated that azulene-containing polyenal analogs of retinal could be incorporated into the important retinal-protein, bacteriorhodopsin. The resulting stable pigments were extremely red-shifted and absorbed deep in the Near IR region.<sup>1</sup> These results provided incontrovertible evidence of the exceptional  $\pi$ -electron donating ability of azulene relative to other heteroaromatic donor groups. At the inception of this project considerable headway had already been made in deciphering the structural requirements of conventional alternant aromatic donors that lead to enhanced optical nonlinearities. However, little was known of the NLO activity of the important class of azulene-containing chromophores.

Our initial goal was to synthesize a series of representative azulene-containing donor-acceptor and symmetrical cyanine dye-like chromophores using well-established synthetic protocols. Thereafter, in collaboration with project scientists and others, we sought to determine and evaluate the effects of structural changes on their nonlinear optical activities. In turn, this feedback enabled us to focus our synthetic efforts on the design of azulenic chromophores with enhanced optical limiting capability to meet the general guidelines set forth for effective eye and sensor protection. In this final report we recapitulate and summarize our research results.

### The $\pi$ -Electron Donor Strengths of Guaiazulene and N,N-Diethylaniline

At the onset it was not at all certain that azulene could function as an electron-donor in NLO donor-acceptor molecules. We therefore sought to determine its donor ability and compare it to amino-substituted aromatics of proven donor strength. In collaboration with V. Pushkara Rao of



ROITech, second-order NLO coefficients ( $\beta\mu$  -values by the EFISH technique) and thermal stabilities of representative azulenic donor-acceptor chromophores were measured together with molecules containing the para-N,N-diethylaminophenyl donor group, keeping the acceptor strengths and spacer lengths constant.<sup>2</sup>

Table 1. Absorption Maxima,  $\beta\mu$ -Values, and Melting Points of **1** - **4**.

Compounds	$\lambda_{\text{max}}(\text{nm})^{\text{a}}$	$\beta\mu$ ( $10^{-48}$ esu) <sup>b</sup>	$T_{\text{d}}$ ( $^{\circ}\text{C}$ ) <sup>c</sup>
<b>1</b>	582	1323	247
<b>2</b>	555	1400	214
<b>3</b>	513	911	290
<b>4</b>	477	906	280

a. in dioxane; b. at 1.907  $\mu\text{m}$ ; c. DSC

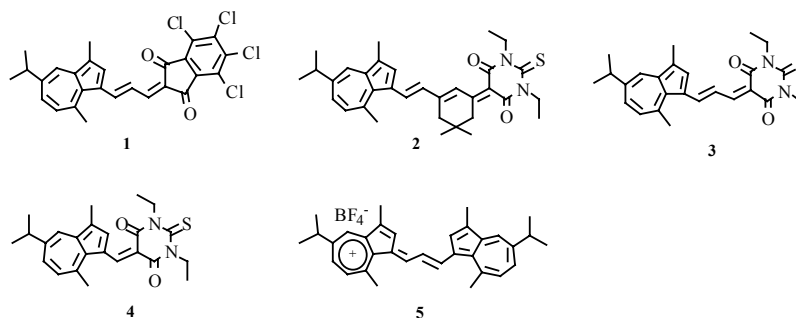
We were gratified to find that the absorption maxima for the azulenic DA chromophores were even more red-shifted than the aniline derivatives and the  $\beta\mu$ -values were not significantly compromised – for both classes of compounds  $\beta\mu$ -values were essentially identical. Moreover, the thermal stability of the azulene derivatives was consistently better than their nitrogen-containing counterparts.

### Theoretical Approaches to Optimizing Azulenic Donor-Acceptor Optical Nonlinearities

A subsequent theoretical study of the NLO properties of azulenic DA molecules revealed several structural design features leading to significant enhancement of first molecular hyperpolarizabilities and  $\beta\mu$  -values.<sup>3</sup> Using AM1/FF and ZINDO/S-CI approaches, the calculated  $\beta\mu$  -values were in close agreement with experimental results. Moreover, when substituted with both donor and acceptor groups on either ring, the azulene molecule was calculated to be a more efficient conjugation bridge than either benzene or thiophene. It was also predicted that azulene derivatives with 1-donor and 5-acceptor groups – so-called *umpolung* molecules with reversed substitution patterns – should have very large second-order coefficients and relatively small dipole moments. Reducing electrostatic interactions is an important goal since it portends increased loading levels and order parameters when incorporated in a suitable polymer matrix.

## First Hyperpolarizabilities of Azulenic Donor-Acceptor Chromophores as Determined by the Hyper-Raleigh Scattering Method at 1907 nm.

In collaboration with C. H. Wang at the University of Nebraska-Lincoln first molecular hyperpolarizabilities for the following azulenic donor-acceptor chromophores were determined at 1064 and 1907 nm excitation wavelengths.<sup>4</sup>



Measurements at the longer wavelength are more technically difficult, but gave more accurate  $\beta$ -values. Furthermore, results from this HRS study suggested the involvement of *more than one* excited state since the data could not be correlated using the widely accepted two-level model (ground state and one excited state).

## The Involvement of Multiple Excited States in the Lowest Optical Transition of Azulenic Donor-Acceptor Chromophores: A Resonance Raman Study

Strong dispersion in the relative intensities of Raman lines for the charge-transfer band of highly polarizable azulenic donor-acceptor chromophores was observed in a collaborative study with Anne Meyers Kelley of Kansas State University.<sup>5</sup> This Resonance Raman study verified the probable involvement of more than one state in the principal electronic transition of the highly polarized azulenic chromophore. A particularly intriguing explanation involves the mixing of the normally very low intensity azulene  $S_1$  band with the charge-transfer transition resulting in a concomitant dramatic increase in intensity. [1,2] In further support of these spectroscopic results, an excited state kinetics investigation to be described later also revealed the presence of additional excited states including a putative twisted intramolecular charge-transfer species. In all cases azulenic chromophores exhibited negligible fluorescence.

## Dipole Moments $\Delta\mu$ and Linear Polarizabilities $\alpha$ for Guaiazulenenic Azo-Bridged Donor-Acceptor Chromophores by Stark Spectroscopy in PMMA.

In collaboration with Hideki Hashimoto of Shizuoka University, Japan, linear polarizabilities and dipole moment changes for a series of relatively weak guaiazulenenic donor-acceptor compounds with fluorinated benzenes acceptors and an azo bridge were determined in a PMMA matrix.<sup>6</sup>

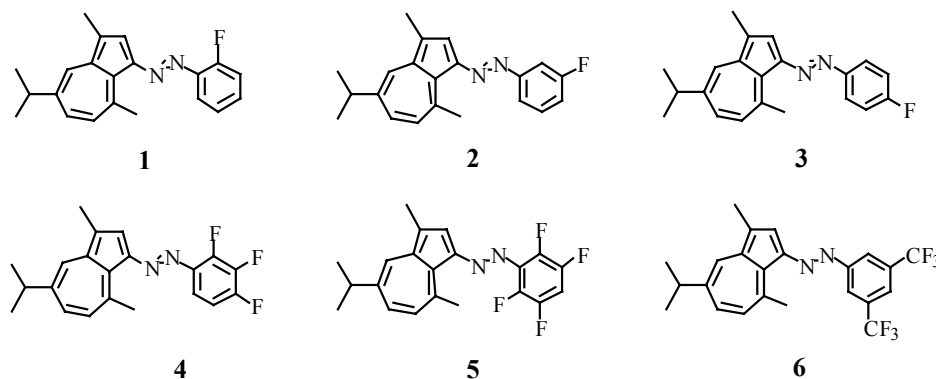


Table 1. Absorption maxima, dipole moments and linear polarizabilities for Chromophores **1-6**.

Compound	$\lambda_{\text{max}}$ (nm), ( $\epsilon$ )	$\Delta\mu$ (D)	$\alpha / 10^{-23}$ esu
<b>1</b>	458 (28,100)	3.6(3)	2.40
<b>2</b>	458 (30,400)	3.6(3)	2.58
<b>3</b>	449 (27,800)	3.5(3)	2.24
<b>4</b>	464 (29,700)	4.0(1)	2.53
<b>5</b>	518 (38,600)	2.79(6)	3.34
<b>6</b>	480 (30,700)	4.5(3)	2.83

The polarization effects were modest – both dipole moment and polarizability changes were quite small and difficult to measure. However, there were consistent trends associated with both the number of fluorine substituents as well as their location on the benzene ring.

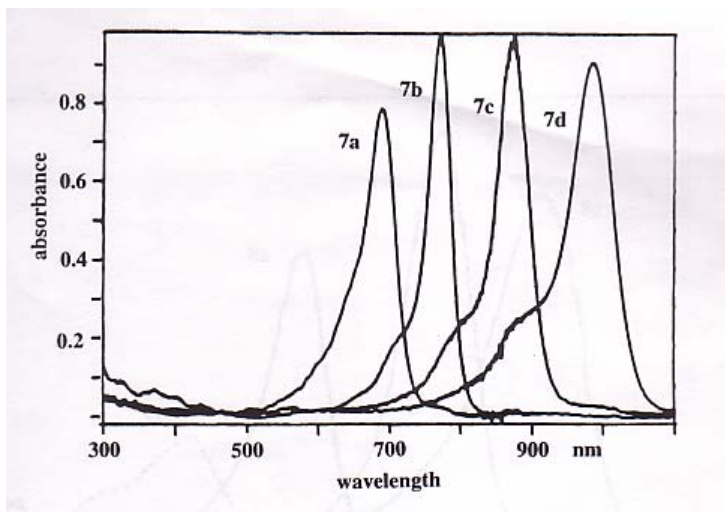
## Azulenenic Polymethine Dyes: Reverse Saturable Absorbers and Optical Power Limiters

In collaboration with Dr. Masato Nakashima of Natick ARO and D. V. Rao of U. Massachusetts-Boston, third-order susceptibilities  $\chi^{(3)}$  were measured for a series of azulenic compounds using the backward DFWM technique.<sup>7-10</sup> From this diverse set of compounds emerged several excellent candidates for optical limiting – the symmetrical guaiazulenenic trimethine dyes. These dye molecules, electronically similar to conventional cyanine or polymethine dyes, are reverse saturable absorbers. Excited state absorption cross-sections were also measured for these compounds by the two-dimensional Z-scan technique.





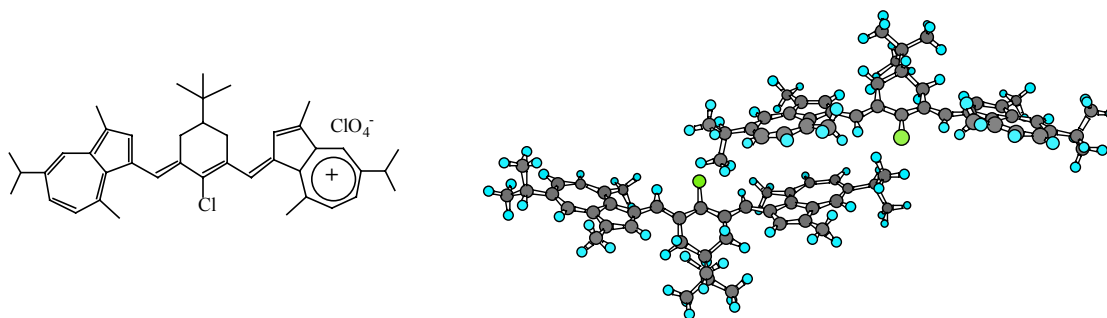
We also measured the electrochemical redox potentials for a many of our azulenic chromophores including the series of dye molecules (data not shown). Representative absorption spectra for dye molecules with 1-4 double bonds are shown below.



Excellent correlation of  $\chi^{(3)}$  values and first and second redox potentials with conjugation length and absorption energies was obtained. In general the dye molecules are stable to light and air in the solid state. The long-wavelength absorbing heptamethine dye partially degrades to a new blue-shifted species upon dissolution in dichloromethane, but in the presence of lithium perchlorate, the solution is indefinitely stable.

#### **A Variable Temperature NMR Investigation of a Prochiral Guaiazulenic Pentamethine Dye: Dimer formation at Low Temperature.**

Aggregation phenomenon – dimerization and H- or J-aggregate formation) – is frequently observed with cyanine dyes and can lead to large optical nonlinearities.<sup>11</sup> We examined the temperature dependent NMR behavior of an intrinsically achiral ring-locked and chlorinated guaiazulenic pentamethine dye and observed unexpected splitting for the isopropyl methyls at low temperature.<sup>12</sup> No signal splitting was observed for dye molecules lacking a prochiral central ring substituent ( $R = \text{CH}_3$  to  $\text{C}(\text{CH}_3)_3$ ); i.e., the prochiral carbon is a prerequisite for chiral dimerization. These observations were in keeping with a model consisting of a nonsymmetrical chiral dimeric “staggered brickwork” assembly, but not with a symmetrical “face-to-face” aggregate.



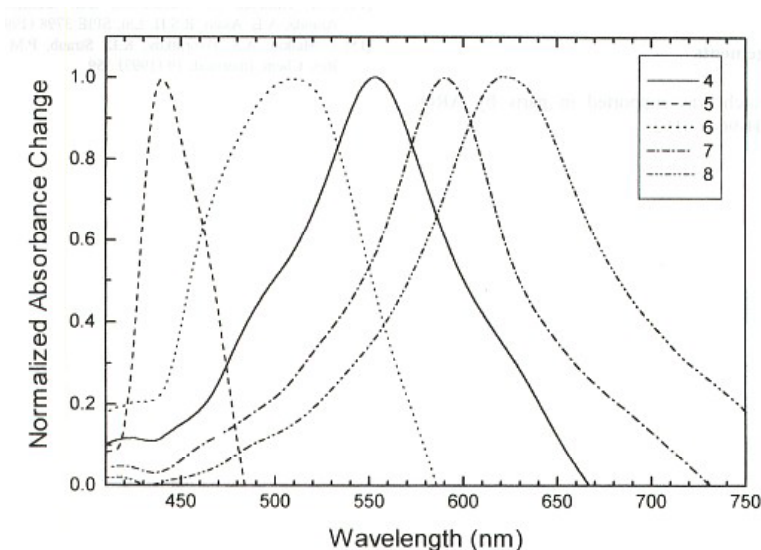
Staggered (brickwork) arrangement

Dimer formation was not observed at low concentrations ( $10^{-4}$ - $10^{-6}$ M) or higher temperatures (RT). No evidence for a dimer was evident in the electronic absorption spectrum.

### **Determination of Excited State Optical and Nonlinear Optical Properties of Azulenic Polymethine Dyes by the Reverse Z-Scan Technique and by Ultrafast Transient Spectroscopy**

In collaboration with Peter Rentzepis of U. California at Irvine, the excited state absorption cross-sections, excited state absorption spectra, and the detailed kinetics formation and subsequent decay of the various excited state species were determined by picosecond transient absorption spectroscopy for a series of azulenic reverse saturable absorber dyes.<sup>13</sup> The salient photophysical properties of the dye compounds were in keeping with excited state requirements for candidate optical limiting chromophores; namely, large excited state absorption cross-sections, broadband spectral response that covers a sizeable portion of the visible region, and extremely rapid sub-psec response times. The ultrafast kinetic response times for the deactivation of the azulenic molecules are probably associated with the novel “breathing” vibration modes localized on the bonds connected to the central ring-fusion bond. These in-plane vibrations in azulene have been calculated to provide a convenient and rapid channel to the ground state via a so-called conical intersection. The sub picosecond excited state kinetic measurements also revealed the involvement of at least three distinct excited state transient species. Upon excitation a very short-lived Franck-Condon  $S_n$  species in an “un-relaxed” solvent cage is initially formed. Rapid solvent reorganization then gives rise to a solvent- equilibrated  $S_1$ . Subsequently, the longer-lived “solvent relaxed”  $S_1$  species undergoes an intramolecular

conformation adjustment to a longer-lived and significantly red-shifted twisted-excited state charge-transfer species. It is this final red-shifted excited state species that ultimately undergoes radiationless decay to the ground state. The normalized excited state absorption spectra of a series of azulenic dyes effectively blankets the entire visible region.

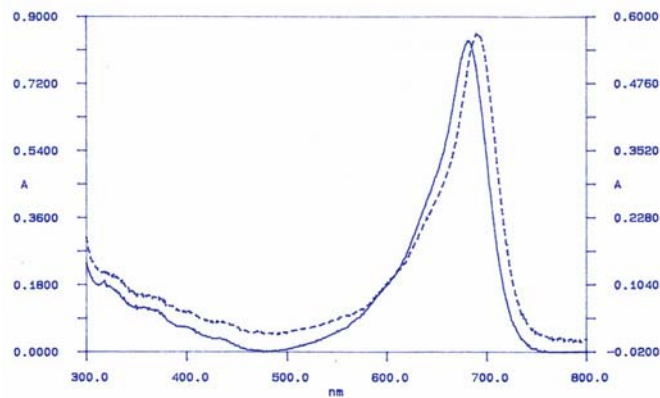


In general, the various excited state transformations of azulenic chromophores are confined to the singlet manifold with little involvement of competing deactivation pathways; i.e., the quantum yields for photoisomerization, intersystem crossing, and fluorescence are essentially negligible.

#### **Polymer Dye Studies: Part A. Guaiazulenic Monomethine Dye in a PSSA Polymer Film**

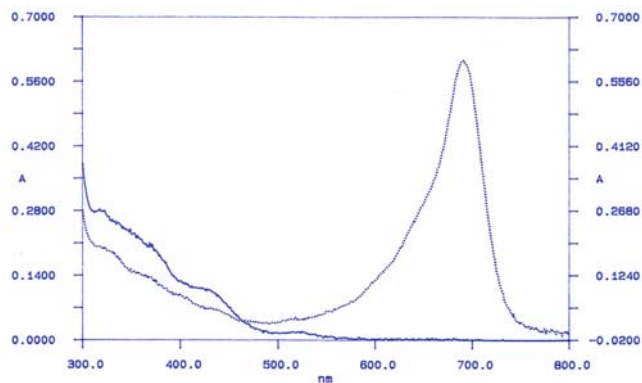
For optical limiting applications reverse saturable absorber dyes must be processible; i.e, the dyes must be thermally stable, resistant to oxidation, non-photobleachable, and soluble in organic solvents for casting into polymer films or fabrication into NLO devices. We investigated the solubility and film-forming characteristics of numerous alkylated azulenic polymethine dyes in PMMA, PS, and other polymer matrixes. Aggregation and separation of the polar dye molecules in both polar and nonpolar polymers was frequently encountered. For an azulenic trimethine dye with long-chain ( $C_{16}$ ) hydrophobic pendant alkyl groups preliminary results suggested liquid crystalline behavior consistent with hydrophobic fatty acid-like interactions of the chromophore.

Polystyrenesulfonic acid, PSSA, is an acidic polyelectrolyte used for coating and other applications. Because our RSA dyes are stable in strong mineral acid, we doped the monomethine dye (structure on page 8) into PSSA, cast an optically transparent film on glass, and recorded its absorption spectra:



Absorption spectra of the monomethine dye in (a) methanol-PSSA solution (solid line) and (b) in a PSSA film on glass (dash line).

The absorption spectra of the green dye solution and the green dye-PSSA film were essentially identical. However, upon brief warming of the dye film it changed from green to tan suggesting the dye chromophore underwent thermally induced bleaching with apparent loss of the chromophore (See below).

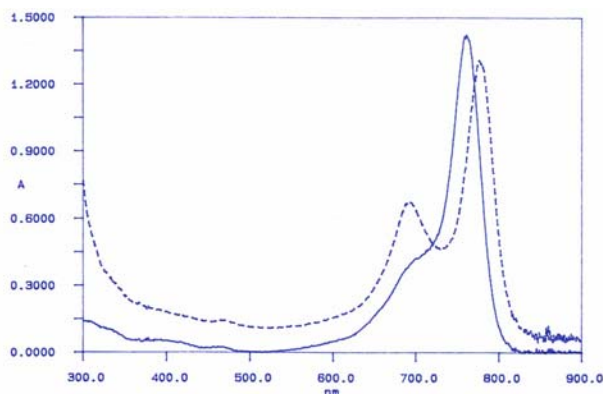


Absorption spectra of a dye-PSSA film sample (a) immediately after "thermal bleaching" (solid line) and (b) after cooling (dotted line).

Surprisingly, upon cooling to room temperature, the green color rapidly returned. The absorption spectrum after one heating-cooling cycle indicated regeneration of the original dye, although the band intensity was somewhat lower (ca. 5%). The optical quality of the film was unchanged after exposure to air and light for several months.

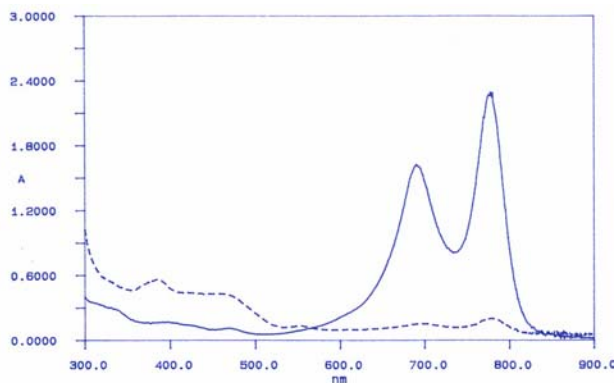
## Polymer Dye Studies: Part B. Unusual Behavior of a Guaiazulenic Trimethine Dye in Acidic and Neutral Polymer Films

We next turned our attention to the next higher homolog, azulenic trimethine dye (structure on page 8). An optically transparent PSSA film was cast on glass and its absorption spectrum recorded.



Absorption spectra of guaiazulene trimethine dye in (a) methanol (solid line) and (b) methanol + PSSA (dash line).

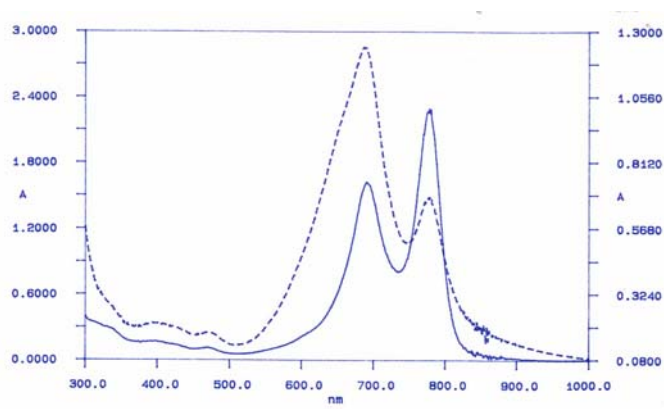
In contrast to the monomethine dye in PSSA a new blue-shifted species (691 nm) was formed in addition to the original dye substrate (760 nm) for the trimethine dye in PSSA. When heated ( $<100^{\circ}\text{C}$  for 1 minute) the trimethine dye-PSSA film reverted from green to tan indicating thermal bleaching. However, upon cooling the sample to room temperature, the 691/760 band had increased (See below).



Absorption spectra of a dye-PSSA film sample (a) immediately after "thermal bleaching" (dash line) and (b) after cooling solid line).

The presence of the 691 nm species suggests the possibility of dye aggregation or thermally-induced formation of the monomethine dye. If the latter process occurred, then its formation

could involve initial hydration of the trimethine dye followed by cleavage to form a stable guaiazulenium carbocation and a highly reactive protonated 3-guaiazulenylpropenal. The latter species could conceivably undergo a retrograde aldol reaction to form a protonated guaiazulene carboxaldehyde intermediate. This species could in turn react with the first-formed guaiazulenium carbocation to give the final product, the stable monmethine dye. The dimer/monomer ratio was also dependent upon the dye concentration with higher concentrations of PSSA favoring the formation of the 691 nm species.

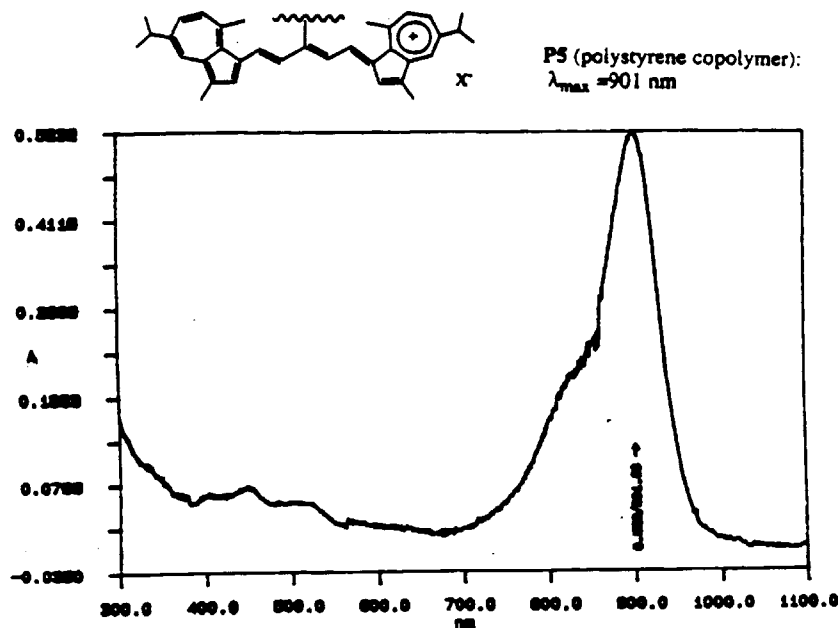


The absorption spectra of two trimethine dye/PSSA films with different dye/PSSA ratios. The dash line corresponds to the higher load level of PSSA.

In contrast to the behavior of azulenic dyes in the strongly acidic PSSA, the same dyes were stable indefinitely in a commercially available neutral polycarbonate co-polymer. Optically transparent polycarbonate films of numerous azulenic dyes were cast on glass. The blue-shifted species was also present in this polymer film. The generation of the high-energy species was not observed in any polymer film in the case of the ring-locked guaiazulene pentamethine dye used in the NMR study described earlier (page 9).

### Polymer Dye Studies: Part C. Formation of a Covalently Bound Guaiazulenic Pentamethine Dye from Polystyrene-*co*-4-Vinylpyridine

The direct incorporation of azulenic dyes into polymers was successfully demonstrated in the preparation of a guaiazulenic pentamethine dye attached to the main chain of a copolymer derived from polystyrene-*co*-4-vinylpyridine) ( $\lambda_{\text{max}} = 901 \text{ nm}$ ). This straightforward synthesis involved the conversion of the pyridine group into a merocyanine dye followed by condensation with guaiazulene to form the desired dye product:



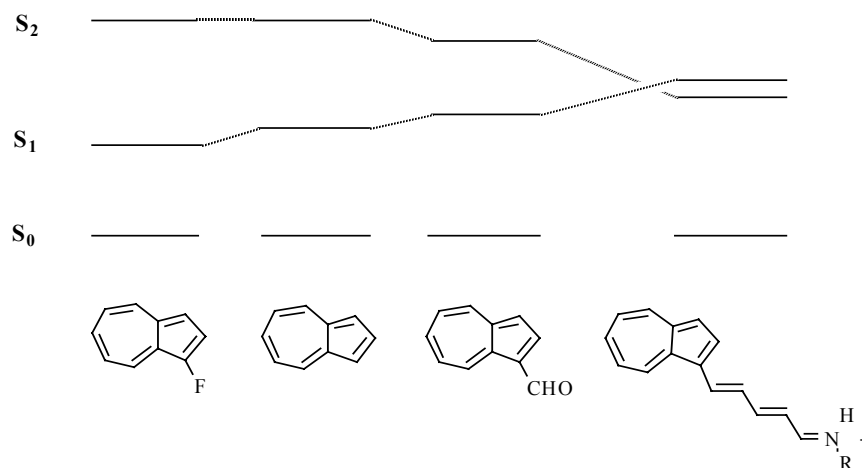
Although we clearly demonstrated the feasibility of preparing a polymer with a covalently attached guaiazulenic pentamethine RSA dye, there remain several obstacles to be overcome; namely, the polymeric dye has limited solubility in dichloromethane and optical-quality films could not be prepared from this material. Optimization of reactant stoichiometry and reaction conditions and the use of alternative 4-vinylpyridine copolymers was not attempted.

### The Manipulation of Excited State Properties of Substituted Azules by Molecular Engineering

We have also investigated in considerable detail the effects of fluorine substitution on  $S_1 \rightarrow S_0$  and  $S_2 \rightarrow S_1$  band gap energies in fluorinated azules.<sup>14-18</sup> It is well known that these band gaps are strongly influenced by inductive and conjugative resonance interactions. While highly



electronegative fluorine is strongly electron-withdrawing through the  $\sigma$ -framework, it is electron-donating in the  $\pi$ -electron framework.



R. S. H. Liu, R. Muthyala, X-S. Wang, A. E. Asato, P. Wang, and C. Ye  
*Org. Lett.* 2000, 2, 269-271.

For instance, examination of the square of the AO-coefficients (localized electron densities) at C1- and C3- of azulene suggest that both  $S_0$  and  $S_2$  energies should be similarly affected by either electron-donation or electron-withdrawal, with  $S_1$  energies changing in just the opposite sense. Thus, a fluorine atom on C1- (or fluorine atoms on both C1- and C3) resonantly destabilizes both  $S_1$  and  $S_2$  to approximately the same extent. Fluorine also destabilizes  $S_1$  by electron-withdrawal and reduction of the excited state dipole moment. The net result is a considerable decrease of the  $S_1 \rightarrow S_0$  band gap ( $S_1$  red shift) and an increase of the  $S_2 \rightarrow S_1$  band gap.

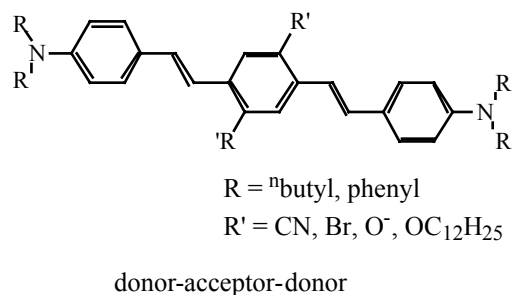
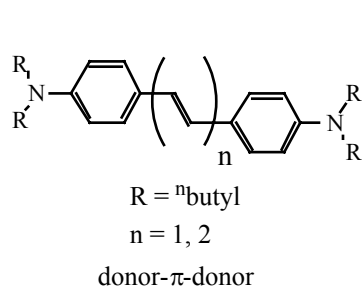
Decreasing the  $S_2 \rightarrow S_1$  band gap results in a color change from blue to purple (azulene-1-CHO) to red (azulene-1,3-diCHO). In contrast, increasing the  $S_2 \rightarrow S_1$  band gap results in a change in color from blue to green to gray-green. Furthermore, the anomalous  $S_2$  emission of azulene is also dependent on the magnitude of the  $S_2 \rightarrow S_1$  band gap with fluorescence quantum yields increasing dramatically with a red shift of  $S_1$ . We observed remarkably large enhancement of fluorescent emission (“a world record”) for the fluorinated azulenes.

Another example of molecular engineering for the enhancement of important photophysical properties was recently demonstrated in our Laboratory for the interesting chromophore, 6-formyl-1,3-difluoroazulene. An electron-withdrawing substituent such as a CHO group attached to either  $C_4$  or  $C_6$  of the seven-membered ring of azulene should stabilize  $S_0$  and  $S_2$ , but destabilize  $S_1$ . Together with the effects of fluorine on the state energies a further narrowing of the  $S_1 \rightarrow S_0$  band gap (a considerable red-shift in  $S_1$  deep into the NIR) and a further widening of

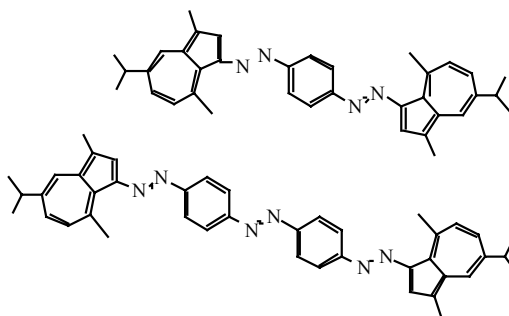
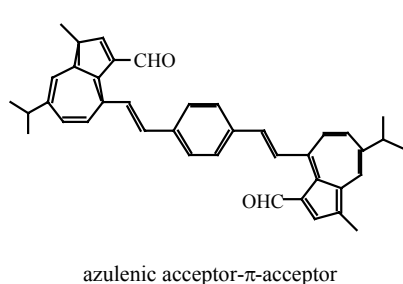
the  $S_2 \rightarrow S_1$  band gap was anticipated. We were gratified to observe the  $S_1$  band of this new chromophore appearing deep in the NIR. Fluorescence studies are currently in progress.

### Azulenic Cross-Conjugated Chromophores as Potential Two-Photon Absorbers

Cross-conjugated chromophores are efficient two-photon absorbers (TPA chromophores) potentially useful for optical limiting and other NLO applications.<sup>11</sup>



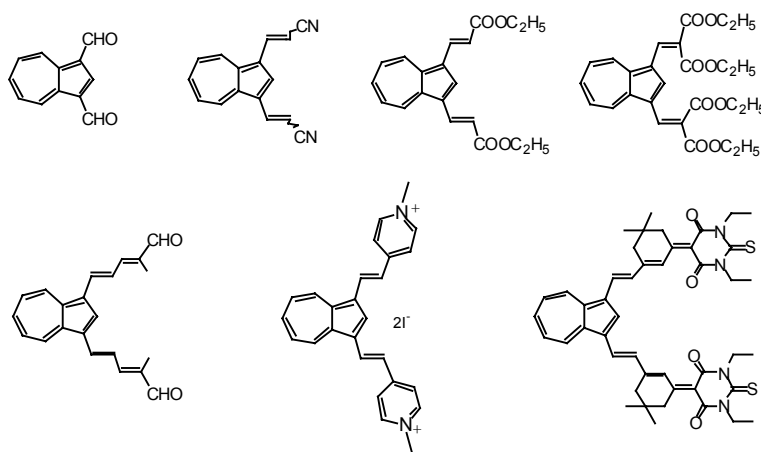
We have prepared a number of centrosymmetric azulenic 2PA molecules with A-D-A and D-A-D structural motifs:



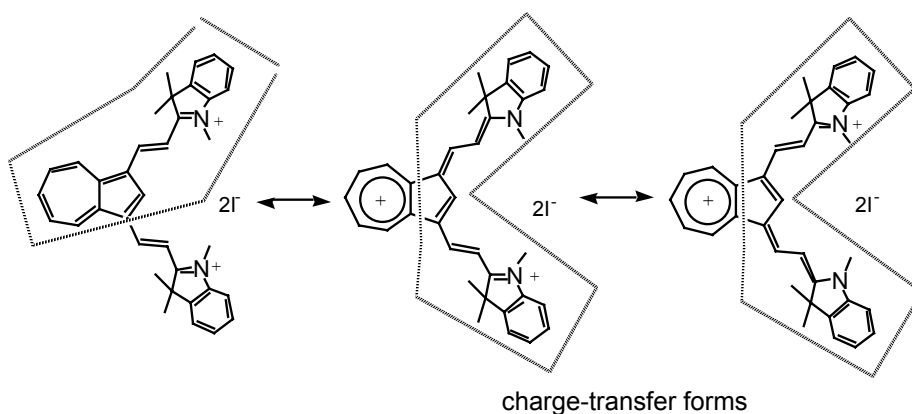
The azulenic A-D-A molecule on the left has the potential of further extension of the chromophore by structural modification of the CHO groups. A relatively compact helical array in which the highly conjugated system folds back upon itself can be easily formed from this interesting molecule. The bis- and tris-azo D-A-D molecules along with non-conjugated bis-azo azulenes exhibit unusual behavior in acidic media: upon protonation spectral shifts up to 171 nm have been realized.

Cross-conjugated alternant aromatic molecules such as meta-disubstituted benzenes always have one resonantly non-interactive substituent (i.e., not participating in charge delocalization). Interestingly, 1,3-disubstituted azulenes are also cross-conjugated and can therefore be categorized as D-A-D chromophores.

A series of cross-conjugated azulenic chromophores –azulene symmetrically substituted with electron-withdrawing groups in both the 1- and 3-positions were prepared for investigation of their potential TPA activity:

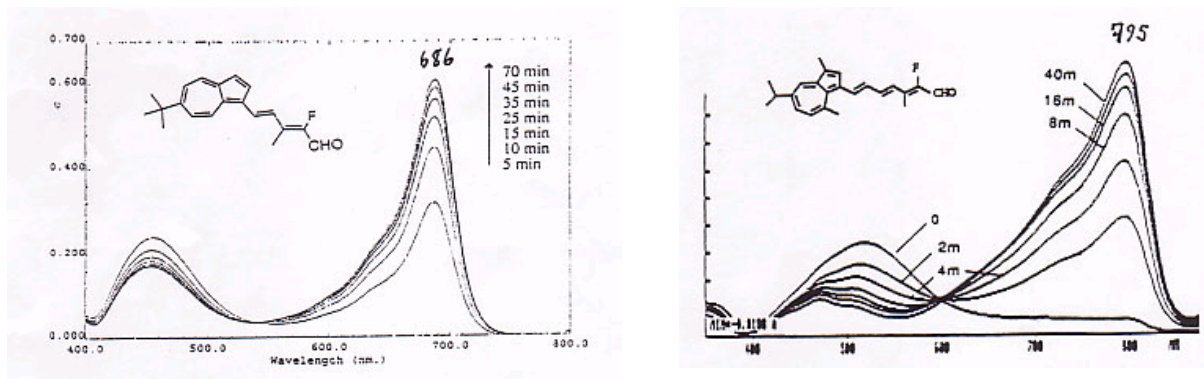


However, in the case of the nonalternant aromatic azulene, a potentially novel situation arises upon charge transfer from the seven-member ring to one of the electron-withdrawing substituents – a new conjugated channel is revealed! That is, a new chromophore orthogonally polarized with respect to the original chromophore is unmasked upon charge delocalization. Such an “unmasking” of a previously unavailable conjugation pathway is not possible in alternant aromatic chromophores, once again confirming the remarkable electronic properties of azulene.



## Long-Wavelength Azulenic Bacteriorhodopsin Analogs as Potential NLO Materials

Bacteriorhodopsin and its mutants has been extensively studied for numerous NLO applications including 3D optical memory devices. The azulenic bacteriorhodopsin analogs are very promising candidate materials for NLO and optical limiting because of their long-wavelength absorption properties, relative ease of binding to the apoprotein, and stability.<sup>1, 19</sup>



The absorption spectra of the most red-shifted analogs – typically intense and reasonably sharp – are similar to that of cyanine dyes. Toward this goal a preliminary investigation in collaboration with Genencor scientists is underway.

## Azulene-Porphyrin Hybrid Chromophores and Upper Excited State Energy Transfer

Excited state energy transfer is of interest both from a purely theoretical viewpoint and from the standpoint of developing new systems for optical switches and other optoelectronic devices. We have synthesized an azulene-porphyrin hybrid chromophore together with several of its metal derivatives. Excited state emission properties are particularly well-matched for this hybrid molecule. Moreover, the acid behavior of the free azulenic porphyrin is in itself quite interesting because it is another example of a cross-conjugated chromophore, potentially useful as a TPA.

## Summary of Research

In this final project report we summarize our results from numerous collaborative studies of the chemical, photophysical, and nonlinear optical properties of several different classes of azulene derivatives: simple azulenic compounds with fluorine and other small substituents, azulenic donor-acceptor molecules, azulenic dyes, and other substituted azulenes. Nonlinear optical properties of both azulene-containing donor-acceptor chromophores and dyes were measured and clearly established their potential utility in optical limiting and other nonlinear optical applications. The effect of fluorine and other substituents on the electronic and photophysical properties of azulene was correlated with molecular orbital properties as well. This discovery allowed us to synthesize very long wavelength-absorbing fluorinated azulenes with remarkably high fluorescence yields.

RSA azulene dye chromophores were incorporated into polymer matrixes by doping or covalent modification of the host polymer. Thereafter, dye-doped polymers were cast into optically transparent films and their spectra recorded. Partially reversible thermochromic behavior with essentially complete thermal bleaching of the chromophore was observed for guaiazulenic dyes in polystyrenesulfonic acid. Aggregation or reversible degradation of a trimethine dye to form the monomethine parent compound was also observed. Dimerization of a ring-locked pentamethine dye was revealed in a variable low-temperature  $^1\text{H}$  NMR study. A joint project in collaboration with Genencor scientists on azulene-containing retinal protein mutants is currently underway.

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- **Report of Inventions**

None

- **Bibliography and Appendixes**

None